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Thiokol CHEMICAL CORPORATION

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NITROSO RUBBER
RESEARCH, DEVELOPMENT AND PRODUCTION.

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FOREWORD

This report was prepared by Thiokol Chemical Corporation under U.S. Army Contract No. DA-19-129-AMC-69(X)O.I. 9044, QMC Project No. 7X93-15-004 with Mr. Frank Babers as project engineer. This report covers work conducted from 1 June through 31 August 1963. The overall project leader is Dr. Marvin M. Fein; divisional project leaders are Mr. Joseph Green at Denville and Mr. Warren Helmer at Trenton. Other contributors to the program are Mr. John Paustian, Dr. Jerome Hollander, Mr. David Kennedy, Mr. Fred Hoffman, Mr. Francis McPeck and Dr. Stanley Tannenbaum at Denville and Messrs. Robert Hoffman and Malcolm Reynolds at Trenton.

ABSTRACT

815
A satisfactory scaleup process for the production of trifluoronitroso-
methane ~~has been~~ developed. The process involves the decarboxylation of
trifluoroacetyl nitrite in refluxing FC-43, $(C_4F_9)_3N$. Copolymerization of
nitroso monomer with tetrafluoroethylene has yielded gums of 300,000-
500,000 average molecular weight. Means of achieving M_n values over
 1×10^6 are under active investigation.

AUTHOR

* to the 6th power



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I. INTRODUCTION

Army-sponsored research oriented toward the development of a chemical and fuel resistant arctic rubber has resulted in the preparation of a 1:1 copolymer of trifluoronitrosomethane and tetrafluoroethylene, generally referred to as nitroso rubber (Ref 1, 2). The nitroso rubber gum stock exhibits excellent solvent resistance, is nonflammable and is resistant to most solvents except those which are halogenated. The glass transition temperature (T_g) is -51°C ; this low T_g value is attributed to rotation of the chain about the N-O bond.

Vulcanizates of nitroso rubber have been prepared; however, even the best of the gum vulcanizates have very low tensile strength. Reinforcement of the vulcanizate with silica filler has resulted in improved, although still not satisfactory, physical properties. Extensive research and development studies have been conducted to investigate the effects of varying the nitroso and olefinic monomers (Ref 3, 4). Terpolymers have been prepared and cured through pendant carboxy groups; the resulting vulcanizates have much greater tensile strength. The cured products continue to exhibit excellent solvent resistance, nonflammability, low temperature flexibility and excellent ozone resistance.

Field evaluation studies have been severely hampered by a shortage of nitroso rubber. Furthermore, the low temperature properties (utility at -40°F) still fall short of the desired serviceability (utility at -100°F) and the relatively low tensile strengths severely limit the usefulness of the rubber. Studies involving monomer variation have not resulted in decreased T_g values to date although terpolymer preparation has resulted in products with improved mechanical properties.

The goals of the present program are fourfold:

- (1) Produce a nitroso rubber with improved mechanical properties
- (2) Produce a nitroso rubber with improved low temperature properties
- (3) Prepare 700 pounds of nitroso rubber for further evaluation
- (4) Fabricate various end items.

Thiokol. CHEMICAL CORPORATION

Thiokol Chemical Corporation has initiated a five-phase R. and D. program to meet these goals:

- (I) Monomer Synthesis and Scaleup
- (II) Polymer Synthesis and Scaleup
- (III) Polymer Production
- (IV) Compounding Studies
- (V) Fabrication

The most immediate problems on the program are to develop practical procedures for production of CF_3NO and for copolymerization of CF_3NO with C_2F_4 . Three paths are possible for attaining nitroso monomer scaleup:

- (1) Develop a new route to CF_3NO which bypasses the trifluoroacetyl nitrite route.
- (2) Develop an improved procedure for decomposition of $\text{CF}_3\text{CO}_2\text{NO}$.
- (3) Develop another nitroso comonomer which eliminates the requirement for CF_3NO .

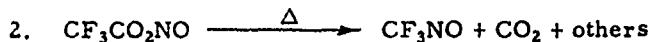
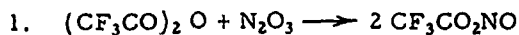
It is obvious that pursuit of (1) and/or (3) will be longer range than (2). Hence, the major laboratory effort during this report period was expended in process development studies for the preparation of trifluoroacetyl nitrite and solution pyrolyses to trifluoronitrosomethane. A safe, reproducible route to the nitroso monomer from the nitrite has been developed. Concurrent with this work, analytical procedures and techniques are being established. Polymerization studies have been initiated both in bulk (-65°C) and suspension (-25°C). Polymers obtained thus far have had average molecular weights in the 300,000 - 500,000 range.

II. TECHNICAL WORK

PHASE I - MONOMER SYNTHESIS

Task 1. Process Development for Trifluoronitrosomethane (CF_3NO)

The objective of this task is the development of a process capable of operation at a production rate of 10 to 50 pounds of CF_3NO per 24-hour period. The process being emphasized, and the one which will be used for initial production, is that involving the pyrolytic decarboxylation of trifluoroacetyl nitrite ($\text{CF}_3\text{CO}_2\text{NO}$).



A. PREPARATION OF TRIFLUOROACETYL NITRITES

Trifluoroacetyl nitrite is being prepared by the interaction of trifluoroacetic anhydride and dinitrogen trioxide (reaction 1, above) and by previously reported techniques (Ref 5). This material is prepared as required for pyrolysis studies and for safety testing. Relatively large quantities are not prepared and stored because of the facility with which it hydrolyzes and oxidizes.

A total of five additional $\text{CF}_3\text{CO}_2\text{NO}$ preparations was completed during this report period with a combined yield of 330 g. The largest single batch prepared to date has been 106 g. The reaction is facile and no difficulty is expected in a several fold scaleup.

As was reported in the previous report, NO is sparged through the reaction mixture to convert excess NO_2 to N_2O_3 . The NO originally used contained an appreciable quantity of NO_2 (14%) and, as a result, it was difficult to follow the course of the reaction by color changes (blue $\text{N}_2\text{O}_3 \longrightarrow$ amber $\text{CF}_3\text{CO}_2\text{NO}$). The more recent experiments used NO of greater than 99% purity and the "end point" of the reaction was more easily determined.

One additional $\text{CF}_3\text{CO}_2\text{NO}$ preparation was completed to determine the feasibility of a preparation in a compatible solvent and thereby reduce the tendency of the nitrite to detonate or to propagate a detonation. FC-43 would be the diluent of choice because of its use in the subsequent decarboxylation, however, the solubility of the nitrite in FC-43 is minimal (<3%); thus, the quantity required would be too great. The trifluoromethyl substituted benzenes are good solvents, and the preparation of $\text{CF}_3\text{CO}_2\text{NO}$ in trifluoromethylbenzene (benzotrifluoride) was found to be facile. Infrared analysis of the product revealed absorption maxima attributable to only the nitrite and the solvent. Reactions of this type and studies of the stability of the solution will be continued if processing with undiluted nitrite is deemed to be too hazardous.

B. SAFETY EVALUATION OF TRIFLUOROACETYL NITRITE

1. Modified Card Gap Test

Data obtained from the Trauzl block testing of $\text{CF}_3\text{CO}_2\text{NO}$ during the last report period (Ref 5) indicated that the liquid can be made to detonate, although the detonation is not very brisant. During this report period, additional detonation testing of $\text{CF}_3\text{CO}_2\text{NO}$ by the card gap test (modified) was begun. The card gap tests involve the determination of whether a sample contained in a tube of a given diameter and composition will propagate a detonation wave from a 50 g tetryl charge and at what rate. Trifluoroacetyl nitrite ($\text{CF}_3\text{CO}_2\text{NO}$) contained in steel tubing up to 5/16 in. ID has been tested; thus far no propagation has been observed. Larger tubes will be used in an attempt to determine the critical diameter for $\text{CF}_3\text{CO}_2\text{NO}$, i. e., the diameter below which no propagation will occur.

2. Ignition Limits

The ignition limits of $\text{CF}_3\text{CO}_2\text{NO}$ were determined over the range of 25 to 100°C as a function of $\text{CF}_3\text{CO}_2\text{NO}$ concentration, nitrogen was used as the diluent. No determinations were made at temperatures greater than 100°C because of the decomposition of the nitrite at these temperatures. The apparatus was evacuable and operated between 50 to 760 Torr, the ignition source was a high voltage spark between tungsten electrodes inside the apparatus. The criterion for ignition was the observance of a sudden pressure increase since the ignitions were not always visible. No detonations were experienced.

The data from these tests are given in Figure 1 (temperature vs concentration) and indicate that $\text{CF}_3\text{CO}_2\text{NO}$ ignites on initiation at concentrations greater

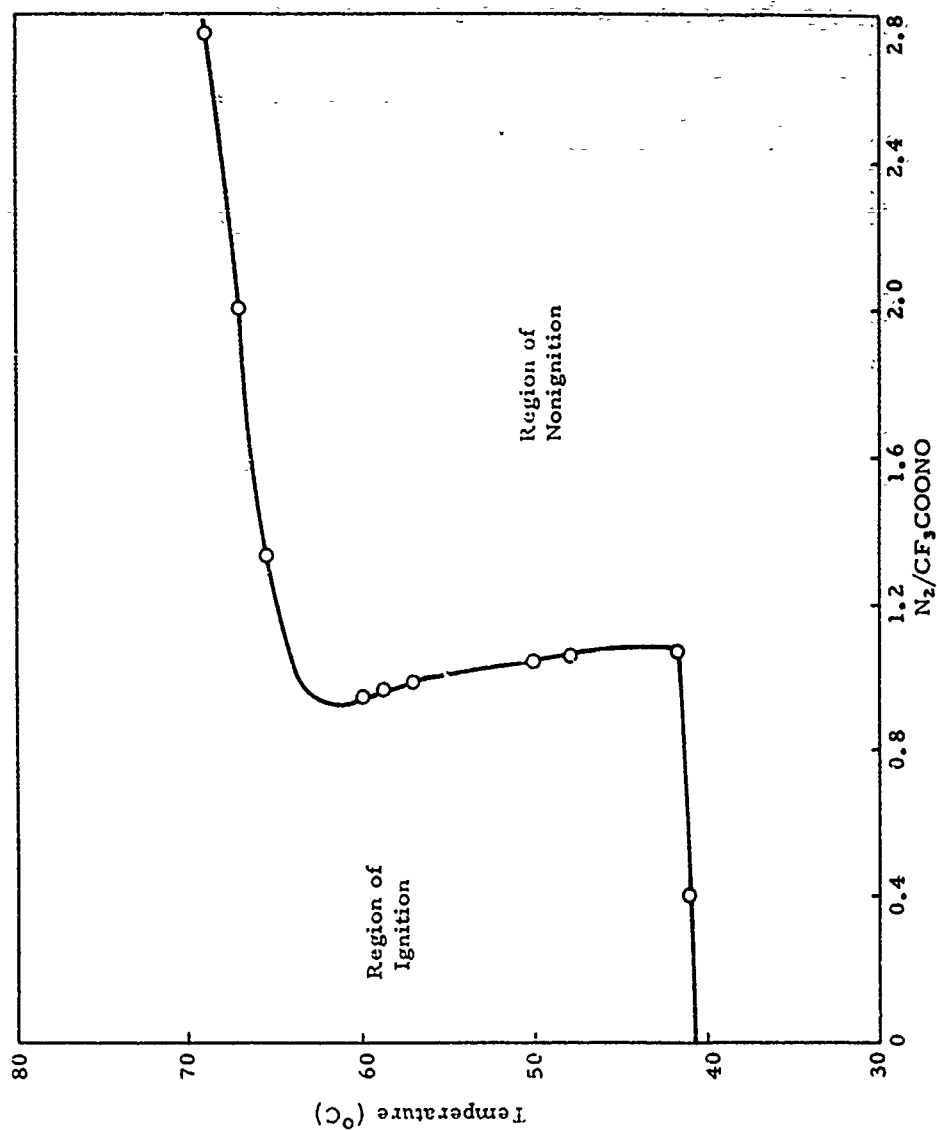


Figure 1. Ignition Limits of Trifluoroacetyl Nitrite in Nitrogen

than 50% up to about 65°C and at lower concentrations at higher temperatures. The lower temperature limit for the ignition of $\text{CF}_3\text{CO}_2\text{NO}$ vapor appears to be about 40°C.

C. PREPARATION OF TRIFLUORONITROSOMETHANE (CF_3NO)

The study of the preparation of trifluoronitrosomethane has been continued at a high level of effort. Although potential alternate methods are being investigated, the bulk of this study has been concerned with CF_3NO formation via the pyrolytic decarboxylation of $\text{CF}_3\text{CO}_2\text{NO}$. All studies were conducted with the goals of maximum safety, product purity, and efficiency of operation. Other routes to this monomer involved the interaction of hexafluoroacetone and nitric oxide, and the interaction of nitrosyl chloride with the difluorocarbene obtained from the decomposition of sodium chlorodifluoroacetate.

1. Reaction .

As has been reported previously (Ref 5), the vapor phase pyrolysis method development at 3M has not been considered because of the technical difficulties required in the scaleup of a reactor with an optimum L/D of 840:1. In addition, the pyrolysis of undiluted $\text{CF}_3\text{CO}_2\text{NO}$, even though at reduced pressures, is considered to represent a detonation hazard. It seemed probable that the tendency for the $\text{CF}_3\text{CO}_2\text{NO}$ to detonate could be modified by dilution if a suitable solvent could be found. FC-43, a 3M product consisting of isomers of $(\text{C}_4\text{F}_9)_3\text{N}$, was investigated and found useful. It has since been utilized exclusively for the pyrolyses to date. Other potential solvents were scanned but not used because of one or more shortcomings, e.g., hydrocarbons (flammability, immiscibility in $\text{CF}_3\text{CO}_2\text{NO}$, and capability of interfering with subsequent polymerizations), and trifluoromethyl-substituted aromatics (too low boiling point). FC-43 has the advantages of nonflammability and apparent nonreactivity toward both $\text{CF}_3\text{CO}_2\text{NO}$ and CF_3NO , coupled with a convenient boiling point, 184°C.

The determination of $\text{CF}_3\text{CO}_2\text{NO}$ decomposition rates under isothermal conditions was continued at temperatures up to the boiling point of FC-43. For these determinations, the nitrite was dropped into the FC-43 at temperature and the evolved gases allowed to expand into a closed, calibrated volume which was large with respect to the quantity of nitrite added. Thus, the system pressure did not rise appreciably over atmospheric. The pressure increase in the system was noted at intervals and plots of ΔP vs time prepared. These are reproduced as Figures 2 and 3. The time at which the rate of pressure increase approaches zero is the time required for complete decomposition

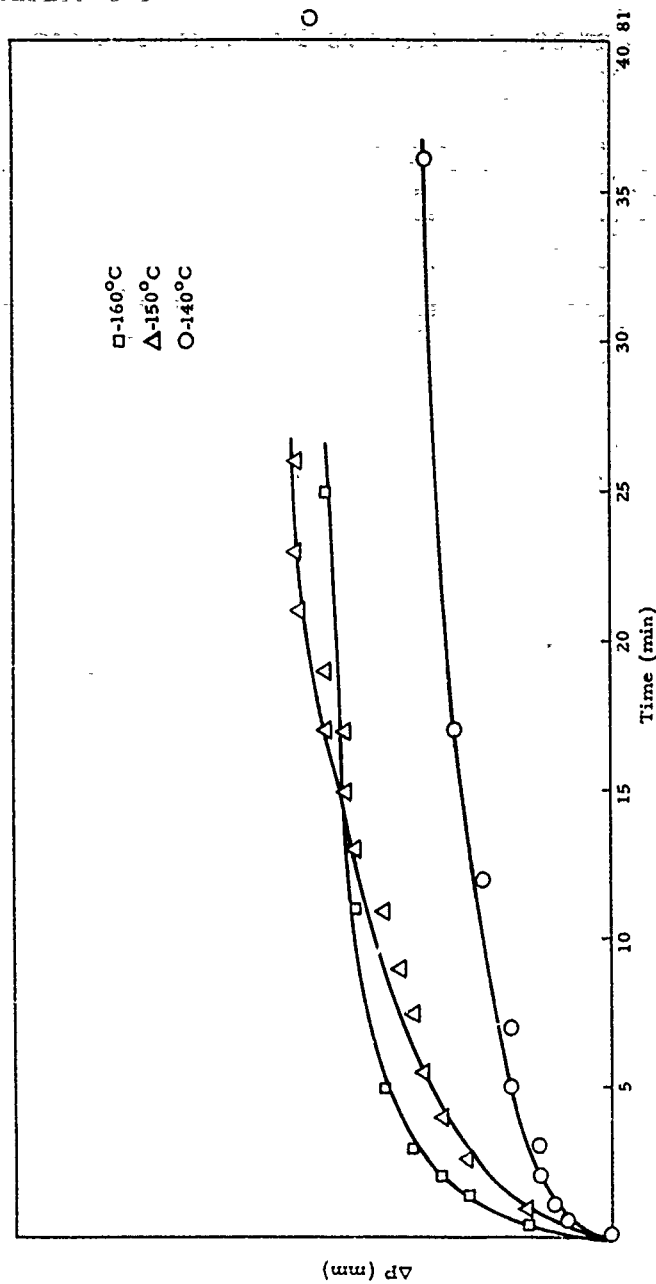


Figure 2. Rate of CF_3COONO Pyrolysis in FC-43

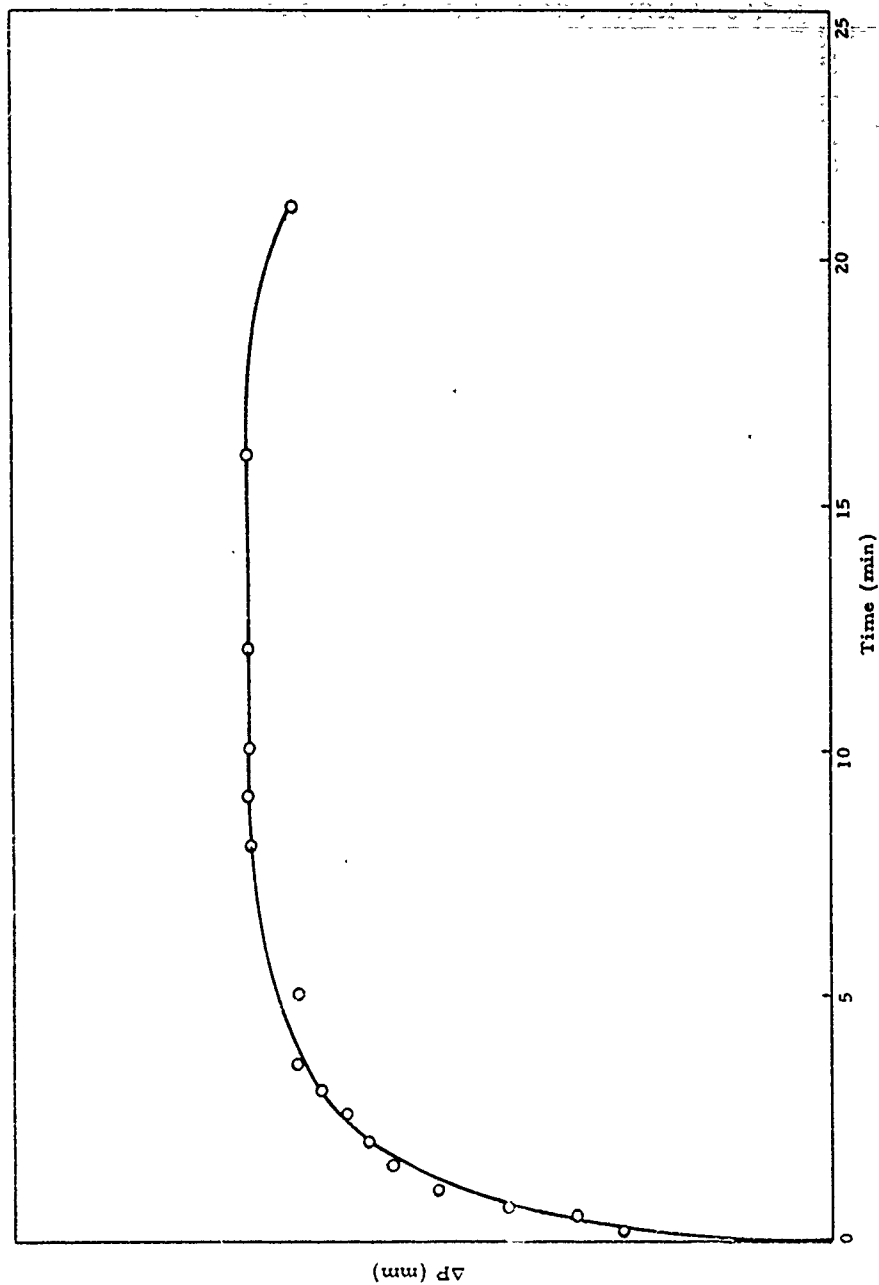


Figure 3. Rate of CF_3COONO Pyrolysis in FC-43 at 184°C

At 184°C , this period is about 5 to 7 minutes, and, at lower temperatures the times are proportionally longer. Although higher temperatures could be obtained by operation under pressure, previous work has indicated that decreased CF_3NO yields and an increased hazard could be expected (Ref 6) at such temperatures. Therefore, it was decided to develop a process at 184°C .

Since at this temperature the nitrite residence time is relatively short, attempts were made to make this process continuous. An apparatus was constructed for a reaction of this type which consisted of a nitrite addition funnel, a reaction flask containing the FC-43 surmounted by a water-cooled condenser, and a purification system terminating in a vacuum line with liquid nitrogen-cooled traps for product collection. In operation, the FC-43 was heated to reflux and the nitrite added at a rate equal to, or less than, the rate of its disappearance by decomposition. A slow helium sweep was introduced for positive displacement of the products and to prevent any possibility of air diffusion into the collection traps. This apparatus was designed as a check of the method and the nitrite charges were normally quite small. Experiments in this apparatus are summarized in Table I. These experiments were successful. Because of the lack of precise analytical data, the calculation of yields has not been possible in most cases. The yield from Exp. 899 was calculated to be 51% as pure CF_3NO , however, it is anticipated that optimum conditions will result in even higher yields. Other experiments were conducted at 165° and 175°C . Product weights were lower and the products appeared to be less pure.

Since these pyrolyses were effected at 184°C , a temperature significantly higher than the boiling point of the nitrite, 99°C , it is probable that the greatest part of the decarboxylation takes place in the vapor phase. Thus, to increase the capacity of the reactor, the vapor phase volume should be increased, not the liquid phase. Since the pyrolysis products are gas phase and since the FC-43 acts only as a heat transfer agent, only enough FC-43 is required to provide one atmosphere of vapor in the reactor and a refluxing liquid phase for nitrite addition. No increase in the liquid phase volume during the reaction will occur. Because the hot FC-43 vapors serve as a diluent for the nitrite vapors, the possibility of the initiation and propagation of a detonation is minimized.

In experiments in which the vapor volume was increased (Exp. Nos. 899 and 900, Table I), it was found possible to add nitrite at a significantly faster rate. Since these reactions were at a small scale and the nitrite was added incrementally through a stopcock, it is not possible to determine the maximum addition rate as a function of reaction volume with accuracy. An apparatus has now been assembled which consists of a one inch diameter

TABLE I
PYROLYSES OF CF_3CO_2NO IN FC-43

Exp. No.	T _{amp} (°C)	CF_3CO_2NO (g)	Time (min)	Purification System	Product Wt. (g)	CF_3NO Content (%)	CF_3NO Yield (%)	Remarks
881	165	3.75	17	H ₂ O + Molecular sieve	1.04	--	--	Prod. contains N oxides.
882	165	3.57	16	H ₂ O + Molecular sieve	1.07	--	--	Prod. contains N oxides.
883	175	3.33	20	H ₂ O + Molecular sieve	0.96	--	--	Prod. contains N oxides.
884	184	3.32	37	H ₂ O + Molecular sieve	1.21	--	--	Prod. contains N oxides.
885	184	3.13	30	H ₂ O + Molecular sieve	1.30	--	--	Prod. contains N oxides.
892	184	6.39	50	H ₂ O + Molecular sieve	2.52	--	--	Prod. contains N oxides.
893	184	26.07	265	H ₂ O + Molecular sieve	10.8	89	53.2	Prod. contains N oxides.
894	184	3.04	39	H ₂ O + MgCO ₃ + Molecular sieve	1.38	--	--	Prod. contains N oxides.
899	184	10.73	68	H ₂ O + MgCO ₃ + Molecular sieve	4.79	79	50.9	Increased vapor volume; Prod. contains N oxides.
900	184	11.07	80	H ₂ O + MgCO ₃ + Molecular sieve	Impure, CF_3CO_2NO swept through.			
851	184	9.26	74	Dry Ice trap, 5% KOH	3.47	--	--	Not analyzed.
863	184	21.41	115	5% KOH	7.57	94	48.0	Increased vapor volume.

adiabatic column two feet long which is mounted on a 100 ml heated flask. It is expected that rate data can be obtained from this reactor with good accuracy and from which data can be obtained for the design of production reactors. Initial experiments with 3 g nitrite charges have been completed in this apparatus and have indicated the feasibility of its design and operation.

Based upon these experiments, a prototype production reactor has been designed. The reactor will be constructed of standard Pyrex pipe with suitable flanges and gaskets. Sizing of each component and final design of the purification system will be completed as data from the current bench-scale reactor is obtained.

2. Purification

Although the major products resulting from the pyrolysis of $\text{CF}_3\text{CO}_2\text{NO}$ are CF_3NO and CO_2 , many other species are produced. These species include N_2O , NO , NO_2 , CF_4 , C_2F_6 , C_3F_8 , C_4F_{10} , COF_2 , CF_3NO_2 , and $(\text{CF}_3\text{NO})_2$. The method for removal of the deleterious impurities recommended by 3M (Ref 3) consisted of a water scrubber, a drying tower, and a molecular sieve (4X) tower to remove the CO_2 . This was the system utilized in the initial pyrolysis runs. It was found, however, that two water scrubbers in series did not completely remove the oxides of nitrogen and that they were ultimately eluted from the molecular sieve column. Thus, contamination of the product occurred. The addition of a weak base (magnesium carbonate) either as a column of solid material or as a suspension in water was not found to reduce NO_2 contamination. Although the use of strong bases had not been recommended because of CF_3NO degradation (Ref 7), the use of 5% aqueous potassium hydroxide in the scrubbers did not degrade the CF_3NO . The KOH scrubbers effected a significant reduction in the NO_2 level. For example, the assay of the product of Exp. 899 (MgCO_3 suspension) indicated 79% CF_3NO , 14% NO_2 , 5% N_2O and the remainder (2%) COF_2 , C_3F_8 , and C_4F_{10} . The product of Exp. 863 (5% KOH) was found to consist of 94% CF_3NO , 5% NO_2 , and 1% N_2O . It is expected that further refinements in the purification system will result in CF_3NO of greater than 99% purity.

Quantitative assay of these products has not been possible until recently because of the time required for calibration of the instruments for each component. Therefore, only rough estimates were available during the time that the majority of these runs were made. The assay of NO and NO_2 was especially difficult since the chromatographic column used for CF_3NO (12 X molecular sieve) cannot separate these compounds. Therefore, assays had

to be obtained from mass spectral data and these figures are considered to be $\pm 2\%$. Mass spectra of "as prepared" CF_3NO samples are given in Table II with that of pure CF_3NO for comparison.

TABLE II
MASS SPECTRA OF CF_3NO

m/e	Ionic Species	Relative Intensities			
		CF_3NO Pure ^a	Exp. No. 899 ^b	Exp. No. 900 ^b	Exp. No. 863 ^b
26	C-N^+	1.2	0.8	0.8	1.2
30	N-O^+	100.0	100.0	100.0	100.0
31	F-C^+	11.0	10.2	8.5	9.2
44	N_2O^+	--	3.6	10.2	5.8
45	F-C-N^+	1.9	2.3	1.4	0.8
46	NO_2^+	--	3.2	5.6	0.8
47	COF^+	--	0.5	1.6	--
50	F_2C^+	15.7	16.4	11.8	11.7
64	$\text{F}_2\text{-C-N}^+$	2.9	2.0	3.2	1.2
69	F_3C^+	36.0	61.5	112.8	35.0
99	F_3CNO^+	1.2	2.7	1.0	1.6
119	F_5C_2^+	--	2.7	--	--
131	F_5C_3^+	--	--	16.8	--
150	F_6C_3^+	--	--	1.6	--
169	F_7C_3^+	--	--	0.3	--
181	F_7C_4^+	--	--	0.1	--
200	F_8C_4^+	--	Masked by Mercury Peaks		
219	F_9C_4^+	--	--	2.9	--
238	$\text{F}_{10}\text{C}_4^+$	--	--	0.8	--
269	$\text{F}_{11}\text{C}_5^+$	--	--	0.1	--

a - Purified by vapor phase chromatography

b - Process-Stream CF_3NO

3. Preparation of CF_3NO by Peninsular ChemResearch

In order that emphasis at RMD be given to process studies, an order for one pound of CF_3NO was placed with Peninsular ChemResearch (PCR). The material was received in increments during this report period and is being used for polymer development studies. This CF_3NO was prepared by replicate vapor phase pyrolyses in apparatus similar to that used at 3M (12 mm dia. tube, 30 ft long); nitrogen was used as the carrier gas. A diagram of the apparatus is shown in Figure 4 and the conditions of the several runs are summarized in Table III as submitted by PCR.

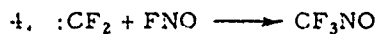
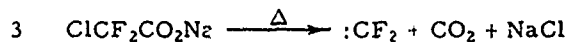
This material was delivered in three shipments with a total of six cylinders. The CF_3NO content of these samples ranged from 85 to 89%; complete analyses are given in Table IV. PCR analyses indicate purities > 96%.

It is noteworthy that the yields of purified CF_3NO by this procedure (6 to 27%) are significantly lower than those obtained by the pyrolysis in FC-43 (up to 53%).

D. NEW PREPARATIVE METHODS FOR CF_3NO

Although the preparation of CF_3NO via pyrolysis of $\text{CF}_3\text{CO}_2\text{NO}$ appears to be facile, the method is not advantageous since one of the starting materials $[(\text{CF}_3\text{CO})_2\text{O}]$ is expensive and the handling and pyrolysis of $\text{CF}_3\text{CO}_2\text{NO}$ represents a potential hazard. Therefore, other methods of preparation are being investigated. Although no new preparative method will be considered for initial production, increased operating economy and safety may be realized in subsequent operations.

One potential method is the interaction of nitrosyl fluoride and sodium chlorodifluoroacetate:



Reaction 3 is known and it was considered that if the difluorocarbene could be generated in the presence of FNO, reaction 4 would take place. FNO is not as yet available, but as a check of the feasibility of the reaction, nitrosyl chloride (ClNO) was used; the product in this case would be chlorodifluoro-nitrosomethane

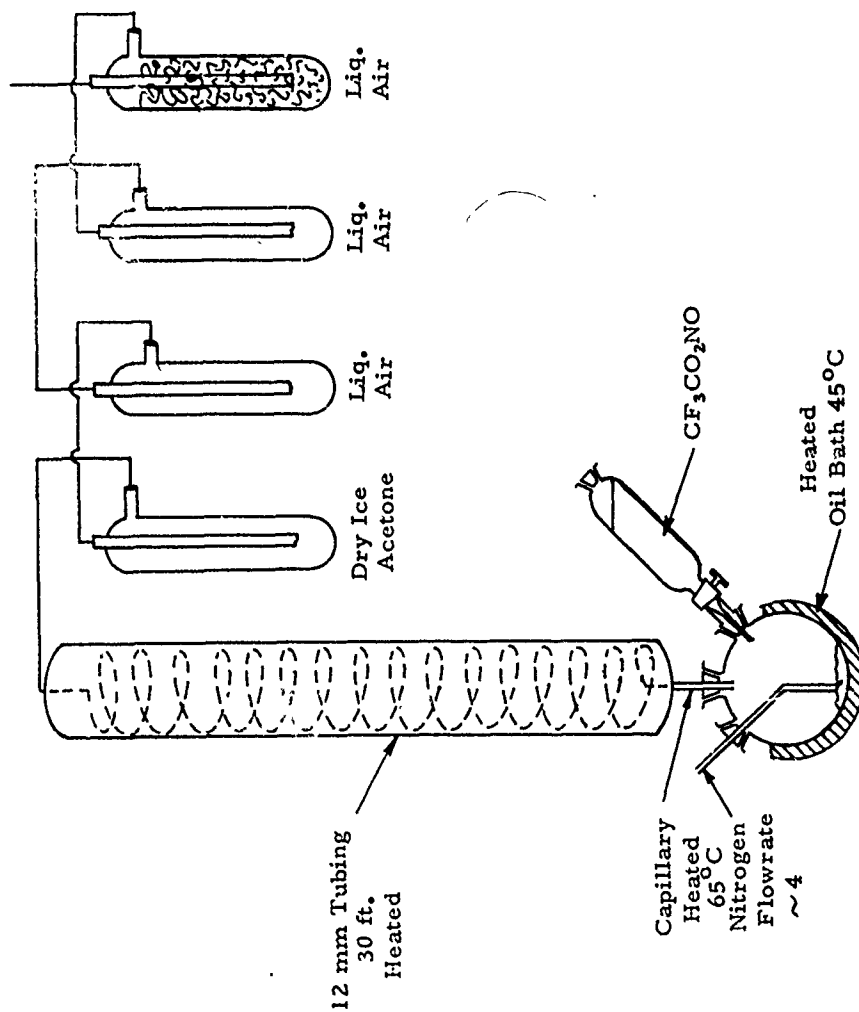


Figure 4. Apparatus used for CF₃NO Production at Peninsular ChemResearch

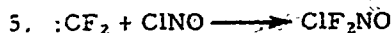
TABLE III
CF₃NO PRODUCED AT PENINSULAR CHEMRESEARCH

CF ₃ NO/ working day (g)	Column Temp (°C)	Pressure (mm)	Pot Temp (°C)	Yield (%)	Comments
4	180	40	60-65	12.7	IR showed C ₂ F ₂ , CO ₂ traces of CF ₃ NO Product contained 50% C ₂ F ₆
traces	160	40	40	--	
2	160	vacuum	40	6.0	
PRODUCTION AT ATM. PRESSURE WITH NITROGEN AS A CARRIER GAS					
--	180	N ₂ Flow 120 ccN ₂ /min		50	Explosion (no explosions were experienced after a heated capillary was in- corporated before the tube)
16	150	1500 ccN ₂ /min	60	14.4	Material collected in liquid air traps con- tained mostly brown- orange material Based on 10 days run (Σ = 270 g)
16	150	1200 ccN ₂ /min	45-60	27	
20	150	1000 ccN ₂ /min	45-60	25	
--	180-200	1500-2000 ccN ₂ /min	60-70		
27	150	1200 ccN ₂ /min	45	23	

TABLE IV
ANALYSES OF PENINSULAR CHEMRESEARCH CF_3NO *

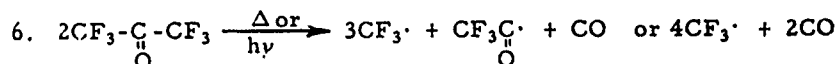
Cylinder No.	CF_3NO (%)	C_2F_6 (%)	N_2O (%)	NO_2 (%)	COF_2 (%)	$\text{C}_n\text{F}_{2n+2}$ (%)	Air (%)
1	86	4	3	7	--	--	--
2	86	4	3	7	--	--	--
3	89	4	1	2	--	trace	4
4	89	4	1	2	trace	trace	4
5	85	--	2	12.5	trace	0.5	--
6	85	--	2	12.5	trace	0.5	--

* RMD analyses. PCR analyses indicate purities of 96 to 98% excluding air.
These discrepancies will be resolved during the next report period.

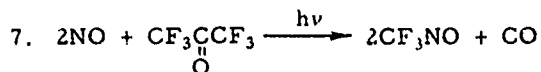


The $ClCF_2CO_2Na$ was prepared by neutralization of the free acid with $NaOH$ and dried at low temperature to prevent decomposition. This material was dissolved in diethyleneglycol dimethyl ether and heated while sparging $ClNO$ through the solution. At temperatures between 95 and $130^\circ C$, a blue color was observed in the effluent gas stream, indicating that $ClCF_2NO$ had been prepared. A white solid, presumably $NaCl$, was precipitated. The gases were passed through a trap at $-76^\circ C$ to remove excess $ClNO$, then condensed at $-196^\circ C$. Mass spectral and infrared analysis of this material indicated the presence of $ClCF_2NO$.

The interaction of hexafluoroacetone and nitric oxide was also studied. Hexafluoroacetone (6FK) is known to decompose pyrolytically and photolytically to give products which are best explained by assuming decomposition as follows:



The synthesis of CF_3NO by photolysis of hexafluoroacetone in the presence of NO has been reported (Ref 8). The only products are CF_3NO and CO .



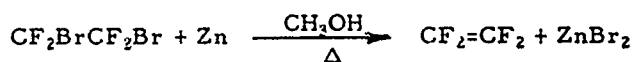
We have attempted to achieve the same goal by a thermal route. One experiment to date involved the passage of a stoichiometric mixture of 6FK and NO through a $1/4$ in. dia. stainless steel tube and allowing a portion of the exit gases to pass into the mass spectrometer. The tube was heated at temperatures to $650^\circ C$, but only 6FK decomposition products (at $> 585^\circ C$) were observed. It is probable that nitric oxide interaction with the steel tube occurred at elevated temperatures and the reaction will be repeated with Pyrex tubing.

Preliminary attempts at photolysis of 6FK/ NO mixtures are in progress; no definitive data have as yet been obtained.

Task 2. Preparation of Tetrafluoroethylene (C₂F₄)

The objective of this task is to prepare or procure sufficient quantities of tetrafluoroethylene for both the initial research studies and for production of the required amount of nitroso rubber.

Tetrafluoroethylene for the production phase of this program will be manufactured in the new Thiokol TFE facilities of the Trenton Division. The amounts required for the initial polymer development tasks are being prepared in the laboratory by the debromination of tetrafluorodibromoethane, Freon 114-B2.



An apparatus for this process has been assembled and put into operation (Figure 5). Tetrafluoroethylene is generated by the controlled addition of the Freon to a refluxing suspension of activated zinc in methanol. The effluent vapors are precooled by a cold water condenser and then passed through a condenser at -35°C to remove any dimethyl ether which may have been produced by a side reaction of zinc and methanol. The product is then condensed at liquid nitrogen temperatures under a slight helium pressure to preclude contamination by atmospheric oxygen. After the reaction is complete, the condensate is warmed to -76°C and transferred in vacuo to a stainless steel storage cylinder containing an inhibitor (Terpene B). Residual material in the -76°C trap has been found to be a mixture of fluorocarbons (including tetrafluoroethylene) and dimethyl ether. This fraction is discarded. These preparations will be completed at the scale and frequency necessary to supply a product for polymerization studies without the necessity for long term storage. A total of four preparations has been completed to date with a combined yield of 48 g. These products have been shown to contain 98.5% C₂F₄, 1.0% C₃F₈ and 0.5% C₂F₆ by mass spectral and chromatographic analyses.

Task 3 New Nitroso Monomers

One of the objectives of this phase of work is to prepare fluorinated nitroso monomers that contain functional groups capable of acting as crosslinking sites for the vulcanization of nitroso rubber. Carboxy-substituted fluorinated nitroso compounds are of interest as termonomers because of the general ease of crosslinking through carboxy groups. Only small quantities of acid

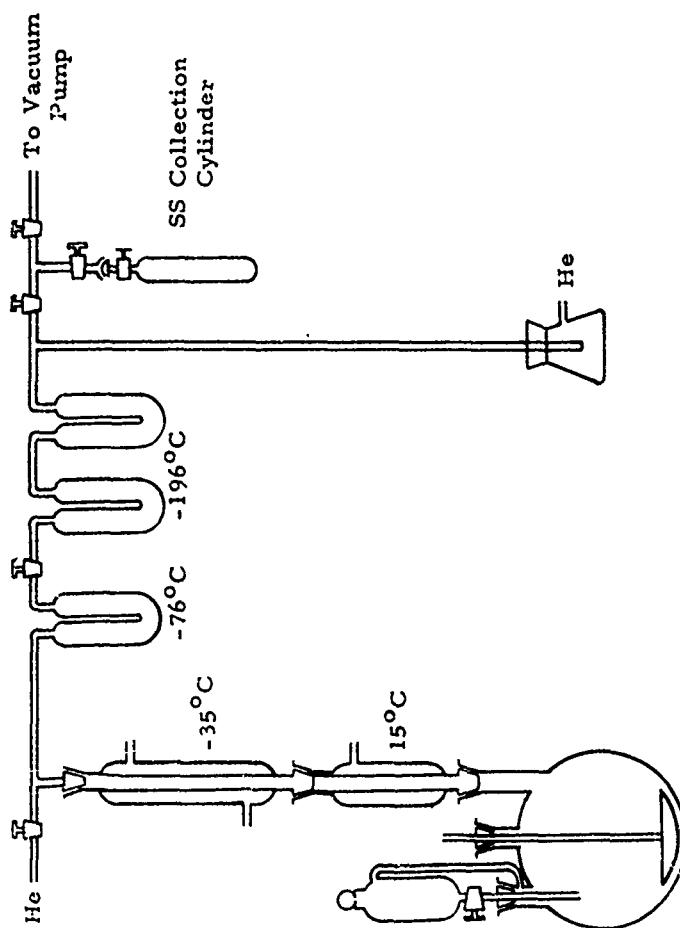
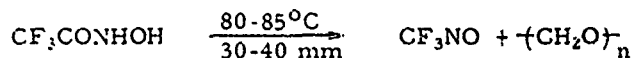
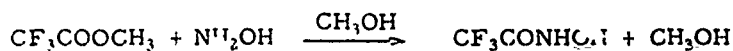


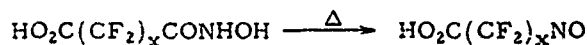
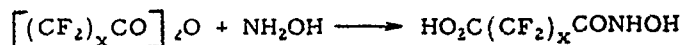
Figure 5. Apparatus for Preparation of C_2F_4

nitroso monomers of unknown purity have previously been prepared by a cumbersome low yield reaction which is not amenable to scaleup (Ref 6).

It was decided to investigate new methods of preparing carboxy-substituted nitroso compounds. The first method chosen for investigation was the preparation and pyrolysis of hydroxamic acids. Knunyants has reported that the pyrolysis of trifluoroacethydroxamic acid, prepared by the interaction of methyl trifluoroacetate and hydroxylamine, gave trifluoronitrosomethane in 63% yield (Ref 9).



Extension of this reaction to fluorinated acid anhydrides should give carboxy-substituted nitroso compounds.



This method was chosen for investigation not only for its feasibility in preparing carboxy-substituted nitroso compounds, but also as a possible alternate route to the preparation of trifluoronitrosomethane.

There is a discrepancy in the literature as to the identity of trifluoroacethydroxamic acid. Pomeroy and Craig reported its preparation by the reaction of trifluoroacetic anhydride with hydroxylamine hydrochloride (Ref 10). These workers report a melting point of 32 to 33°C as compared to 75 to 76°C for the material prepared by Knunyants and coworkers. Both groups of workers reported essentially the same elemental analyses.

Attempts to repeat the work of both groups in these laboratories has met with partial success. The reaction of trifluoroacetic anhydride with hydroxylamine hydrochloride yielded a low-melting hygroscopic solid, similar to that reported by Pomeroy and Craig. Decomposition of the product gave a very small amount of green gas ($\text{CF}_3\text{NO} + \text{N oxides?}$) which was lost

before it could be identified. The reaction has been repeated handling the product under anhydrous conditions, and the pyrolysis will be conducted shortly. Elemental analyses which check with the desired trifluoroacethydroxamic acid have not as yet been obtained.

Treatment of methyl trifluoroacetate with hydroxylamine yielded a white crystalline solid which melted at 72 to 75°C (mp 75 to 76°C reported by Knunyants). The elemental analysis, however, did not check with that reported by the Russian workers. Decomposition of this solid gave only one identifiable volatile product, N₂O, which was identified by its infrared spectrum.

The reaction of trifluoroacetic anhydride with hydroxylamine has also been run; the products of the reaction are currently being isolated.

PHASE II - POLYMERIZATION STUDIES

The objectives of this phase of work are: (1) to conduct polymerization studies to develop capabilities of producing CF₃NO/C₂F₄ copolymer in quantities of 10 to 50 pounds per 24 hour period and (2) to conduct polymerization studies with the new monomers developed under this project, purchased or supplied by the Government.

The trifluoronitrosomethane used in these polymerization studies were either prepared in these laboratories (under the process development studies) or purchased from Peninsular ChemResearch (1 pound). All the tetrafluoroethylene used in this work was prepared in these laboratories as previously reported. Both suspension and bulk polymerization studies have been initiated during this report period.

Aqueous suspension polymerizations were conducted in sealed 30 cc Carius tubes at -25°C in amounts ranging from two to four grams of total monomer weight. Carius tubes were charged with 15 ml of saturated lithium bromide solution (53 g LiBr/100 g H₂O) and 0.5 g of magnesium carbonate which was used as the suspending agent. The tubes were attached to a calibrated vacuum rack and degassed. Accurately measured volumes of CF₃NO and C₂F₄ were charged into the tubes in equimolar quantities. The tubes were sealed under vacuum and placed in a shaker assembly contained in a freezer maintained at -25°C. After 20 hours the tubes were opened and the product was washed three times with distilled water. The coagulated polymer was further washed with concentrated hydrochloric acid until gassing ceased and then washed with water before drying in a vacuum oven. The experimental data are summarized in Table V.

TABLE V
SUSPENSION POLYMERIZATIONS OF TRIFLUORONITROSOMETHANE AND TETRAFLUOROETHYLENE^(a)

Number	CF ₃ NO Source	Mole Ratio	Total Charge, (grams)	Yield, (grams)	% Conversion	Reactant ⁸ /H ₂ O	$[\eta]$	Observations
167084	Peninsular, Sample No. 2	1/1	1.92	1.2	63	1/8	0.34	White gum - poor suspension.
167085-1	Peninsular, Sample No. 2	1/1	3.65	---	---	1/4	---	Tube exploded.
167085-2	Peninsular, Sample No. 2	1/1	3.55	2.6	73.6	1/4	0.44	White gum, sample fractionated to give $[\eta] = 0.62$.
167085-3	(167885)	1/1	1.66	---	---	1/8	---	Broken when 167085-4 exploded.
167085-4	(167893)	1/1	3.50	---	---	1/4	---	Tube exploded.
167086-1	(167893)	1/1	2.02	1.1	54.4	1/4	---	White gum, agitated with steel ball.
167086-2	(167893)	1/1	1.97	1.6	81.0	1/4	---	White gum

(a) 20 hours at -25°C

Viscosity studies were conducted on two of the polymers dissolved in EC-43. Intrinsic viscosities of 0.34 and 0.44 corresponding to molecular weights under 500,000 were obtained (Figures 6, 7 and 8). The second sample (0.44) was fractionated by dissolution in a mixture of fluorocarbon solvents followed by precipitation with acetone. The gum fraction accounted for 85% by weight and the remaining product was a viscous oil. The intrinsic viscosity of the gum was 0.61 (Figure 9).

The relatively low molecular weight of the nitroso rubber gums obtained to date are substantially lower than those which have been reported as obtainable (Ref 2). At the time these polymerizations were conducted, the purity of the CF_3NO had not been determined and monomer ratios could not be adjusted. Analytical studies now available indicate that the CF_3NO prepared both in these laboratories and by Peninsular ChemResearch contained substantial quantities of nitrogen oxides.

Twelve bulk polymerizations of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ are currently in process. The polymerizations are being conducted in sealed Carius tubes maintained at -65°C in a freezer. Several batches of both Peninsular and Thiokol-prepared CF_3NO are being evaluated in a one-to-one molar ratio with C_2F_4 .

PHASE III - PRODUCTION OF NITROSO RUBBER

The objective of this phase of work is to supply the Government with 700 pounds of nitroso rubber of which all or part may be the copolymer $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$. Production is not scheduled to begin before February 1, 1964; in order to maintain this schedule, the design and procurement of equipment has now been initiated. The monomer processes have been defined allowing preliminary reactor design and component procurement. The definition of the polymer processes are expected by October/November 1963.

PHASE IV - COMPOUNDING AND CURING STUDIES

The objective of this phase of work is to conduct studies and evaluations to establish by formulation studies the best methods of realizing the unusual properties of nitroso rubber. Compounding and curing studies are scheduled to begin as soon as a sufficient quantity of polymer is available.

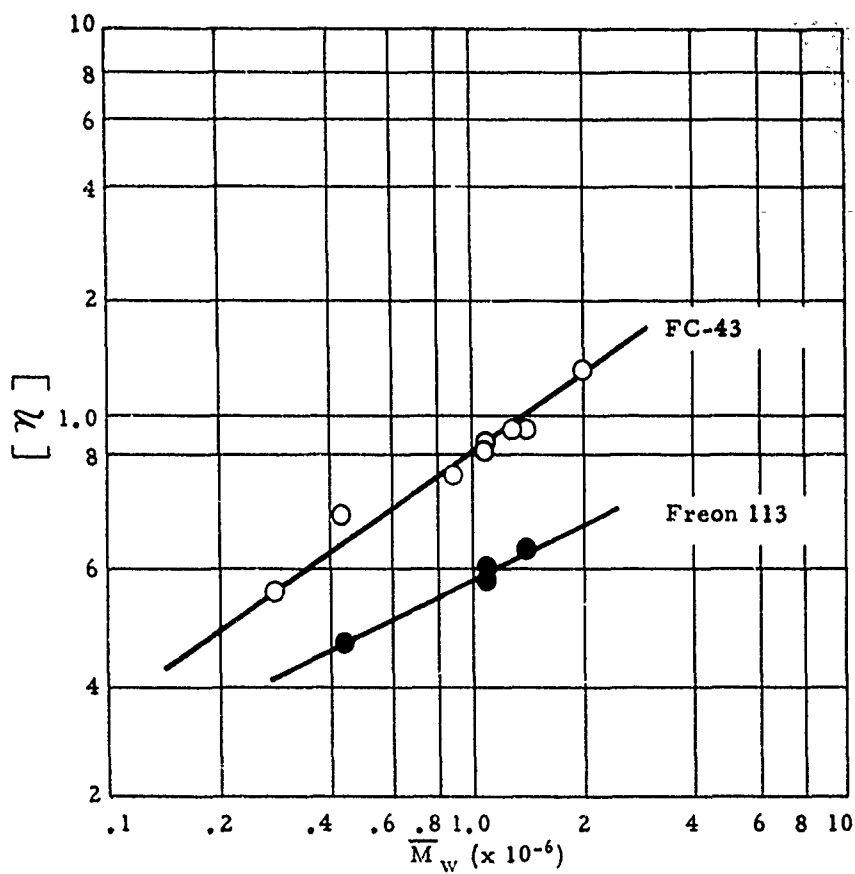


Figure 6. Molecular Weight vs Intrinsic Viscosity for $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Elastomer (Reference 3)

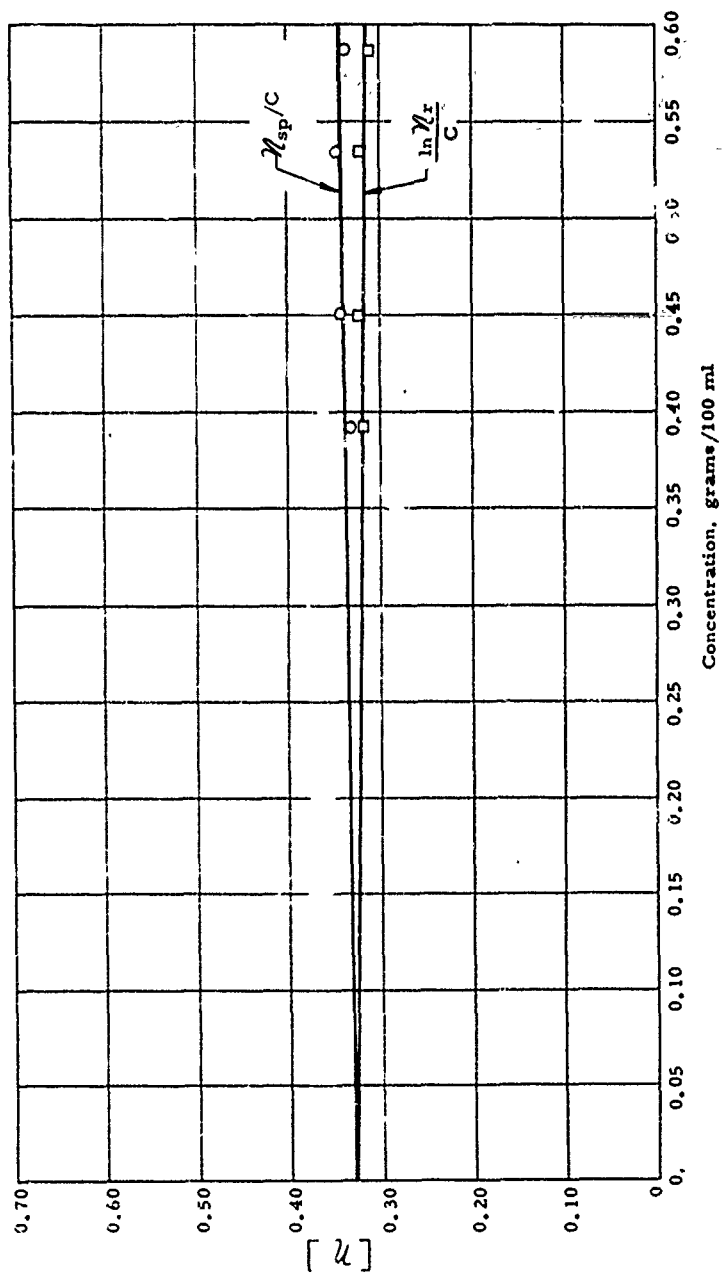


Figure 7. Reduced and Inherent Viscosity Curves for Sample 167084

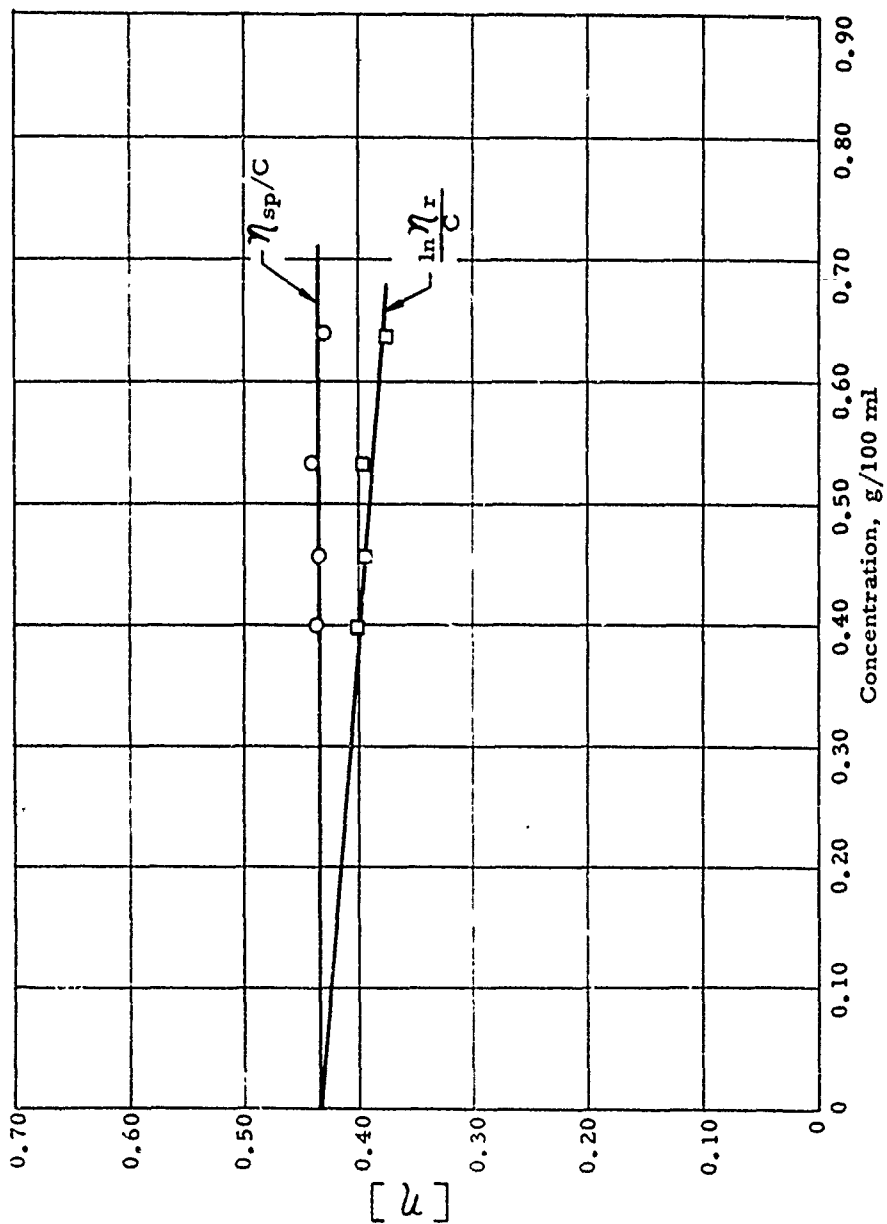


Figure 8. Reduced and Inherent Viscosity Curves for Sample 167085-2

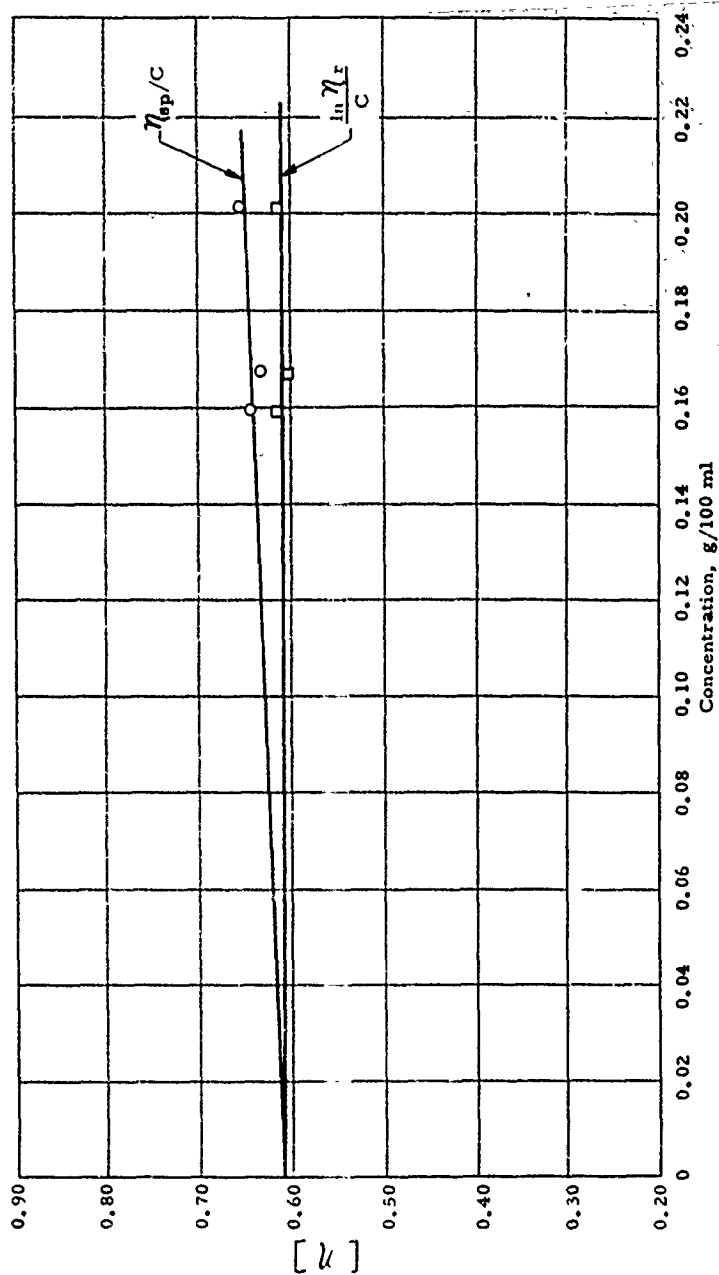


Figure 9. Reduced and Inherent Viscosity Curves for Fractionated Sample 167085-2

PHASE V - FABRICATION

The objectives of this phase of work are: (1) to conduct studies toward developing specific compounds of nitroso rubber that can be used in extrusions, moldings and proofed goods and (2) to produce gaskets, reinforced hose and coated fabric. This phase is scheduled to begin around August 1964.

III. SUMMARY

1. The preparation of trifluoroacetyl nitrite in replicate batches was continued with batch sizes up to 106 g.
2. The critical diameter for trifluoroacetyl nitrite has been determined to be greater than 5/16 inch with metallic confinement. Ignition limits of the vapors were determined over the range of 25 to 100°C as a function of concentration.
3. The rate of thermal decomposition of trifluoroacetyl nitrite was determined for temperatures up to 184°C. At that temperature, the time required for complete decomposition is in the order to 5 to 6 minutes.
4. The preparation of trifluoronitrosomethane by the pyrolysis of trifluoroacetyl nitrite in solvent has been replicated with success. Product yields up to 53% have been realized and purification techniques have been improved. The framework for a continuous process has been defined.
5. Tetrafluoroethylene has been prepared in replicate batches by the debromination of tetrafluorodibromoethane.
6. Several small batches of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer have been successfully prepared by the suspension method.
7. The intrinsic viscosity of two FC-43 polymer solutions are 0.34 and 0.44. Fractionation of the latter polymer yielded 85% of a gum with an intrinsic viscosity of 0.61. The relatively low molecular weight of the polymers has been attributed to impurities in the CF_3NO .
8. Twelve bulk polymerizations are currently in process.

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